Bulletin 622

UNIVERSITY OF FLORIDA
AGRICULTURAL EXPERIMENT STATIONS
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GAINESVILLE, FLORIDA

(A contribution from the Citrus Experiment Station in cooperation with the Florida Citrus Commission)

CITRUS VINEGAR

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AGRICULTURAL EXPERIMENT STATION
GAINESVILLE, FLORIDA

Group 170

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July 1960

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ROBERT R. MCNARY and MARSHALL H. DOUGHERTY[1]

INTRODUCTION

In this country, the traditional raw material for vinegar production has been apple juice or cider. Cider vinegar is the standard with which other vinegars are compared for flavor and cost. Within the last decade or two, the commercial production of wine vinegar has shown considerable growth. While the volume is not yet large compared to cider vinegar, it is sold at a considerably higher price, exclusively for table use. In view of this, it was decided to examine the possibility that citrus juices and by-product liquids could produce vinegars of competitive quality and cost. The investigations described in this bulletin were designed to answer these questions.

Prescott and Dunn (*2*) and bulletins of the United States Department of Agriculture, both early (*3*) and recent (*4*), mention oranges as one of the many possible raw materials for vinegar making. However, the authors have been unable to find reference to commercial production. Difficulties with the development of off-flavors and the obtaining of a clear, stable product may have discouraged earlier workers. Also, the fact that citrus juices, in general, have insufficient sugar to yield a vinegar of at least 4 percent acetic acid (the minimum requirement) may have further contributed to a lack of interest. Since the development of commercial, frozen orange concentrate, orange juice of almost any concentration and amount can be readily obtained. If desired, 100 grain (10 percent acetic acid), or stronger, vinegar now can be made from concentrated orange juice that has been adjusted to the proper concentration.

THE VINEGAR PROCESS

Vinegar making is a 2-step process. Sugars are first fermented by yeasts to an alcoholic liquor, which is then converted into vinegar by acetic acid bacteria. The yeast step is essentially anaerobic in nature and decreased yields of alcohol result from contact with air. On the other hand, air is necessary for

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the oxidation of the alcohol to acetic acid by the bacteria in the second step. The 2 steps therefore must be carried out separately in different equipment and, if desired, they may be performed with extended intervals between them. As a matter of fact, in making cider vinegar it is customary to crush the apples and ferment the juice with yeast as rapidly as possible during the 6 or 8 weeks that ripe apples are available, but to store the fermented juice and make into vinegar during the remainder of the year.

There are 3 main processes by which the alcoholic liquor can be converted into vinegar. They are the slow or Orleans process, the generator process and the submerged fermentation process. All 3 have been used to produce citrus vinegar. They differ in their speed of conversion which is directly related to the rate at which oxygen from the air can be absorbed by the bacteria and utilized.

The Orleans Process.—The slow or Orleans process utilizes a shallow vessel containing the acetifying liquor. The vessel has an opening at the top to admit air. This opening should be screened to exclude insects. The vinegar bacteria grow in a film on the surface of the liquor in contact with the air. Since the acetification activity takes place in this film, the rate of acetification is limited by the relative area of the film. In comparison with the other processes, the rate of vinegar production by this means is very slow. However, the quality of the product is excellent. The efficiency of conversion of alcohol to acetic acid is somewhat less than the other processes. Since it requires little attention, this procedure is favored when small amounts of vinegar are being produced.

The Generator Process.—Faster conversion of the alcohol can be obtained by increasing the contact among the alcoholic liquor, acetic acid bacteria and oxygen from the air in a generator type fermenter. In this fermenter, which has been in commercial use for over 100 years, the liquor is trickled down through a tower packed with beechwood shavings. The bacteria attach themselves to the shavings. Their acetification activity produces heat, which causes a continuous updraft of air through the generator. By this means the necessary oxygen is supplied for oxidizing the alcohol. The liquor reaching the bottom is returned to the top for another passage over the shavings. This is continued until practically all of the alcohol is converted to

acetic acid. The finished vinegar is drawn off and stored in the absence of air. Otherwise the bacteria, in the presence of oxygen, will destroy the acetic acid that they have just produced.

The Submerged Fermentation Process.—This process differs from the other 2 in that the bacteria are uniformly distributed throughout the liquid being acetified. Oxygen is supplied for the oxidation by dispersing air in fine bubbles throughout the liquid. Vigorous agitation accompanies, and is necessary to, the dispersion.

The process was developed first in Europe but has been improved to a high level in this country within the last 3 years (*1*). The more intimate contact among oxygen, bacteria and the acetifying liquid speeds up the acetification activity. Furthermore, the conversion of alcohol to acetic acid in the submerged fermentation comes closer to theoretical values. Ninety-eight percent conversion has been achieved in a properly operated fermenter, which may be compared with 80 to 88 percent conversion in a packed generator and 70 to 80 percent in the Orleans process. The economic implications of the much improved efficiency of the submerged fermentation are obvious.

The more rapid acetification by submerged fermentation demands closer control of the 3 major factors that influence the acetification activity, namely the rate of feeding the wine, the rate of aeration and the temperature. Since the fermentation generates its own heat, it is relatively simple to control the temperature by regulating the amount of cooling water passed through a coil in the fermenter. This is usually done automatically.

The rate of feeding the wine, or mash as it is sometimes called, must be adjusted closely to the activity of the bacteria present. At present this is not subject to automation. The decision of whether to increase or decrease the feed rate must be made from the results of frequent determinations of the percentages of acid and alcohol in the fermenter liquid. The feed rate must be adjusted closely to the activity of the bacteria, or the optimum alcohol concentration will not be maintained.

In a similar manner, the rate of aeration must also be correlated with the activity of the bacteria. Too little air starves the vinegar bacteria and too much air inhibits their activity. The effect of changing the aeration rate on the acid production is the basis for determining the optimum rate.

EXPERIMENTAL PROCEDURE AND RESULTS

The Alcoholic Fermentation.—Before vinegar can be made, the raw material must first undergo an alcoholic fermentation with yeast. The first few batches of citrus vinegar were made from juice that was fermented with a strain of Hansen type wine yeast. It has been established that the strain of yeast does not appreciably affect the quality of the vinegar. Consequently, with the exception of the few batches mentioned, all of the citrus vinegar was made from wine fermented with Baker's yeast purchased in dry form at a nearby grocery. With adequate inoculation the yeast fermentation proceeds quickly and is about complete in 3 days. In 4 to 6 days the yeast has settled and the supernatant wine may be drawn off and filtered. This operation should not be delayed more than 2 or 3 days; otherwise off-flavors may develop.

The Acetic Acid Fermentation.—The first vinegar produced in this laboratory was made in a packed generator. The generator consisted of a glass tube 2.75 inches in diameter and 23.5 inches long filled with beechwood shavings. The alcoholic liquor was pumped to the top of the generator by means of a Sigmamotor pump, which was adjusted so that the feed rate was virtually drop by drop (4.9 ml. per minute). The partly acetified liquor emerging at the bottom was caught in a 500 ml. bottle and returned to the top of the generator by the pump. When the acetic acid concentration reached a maximum, some of the vinegar was drawn off and a like amount of alcoholic liquor was added in its place and the process was continued.

The air needed for the bacterial oxidation was obtained from the compressed air supply in the building. This permitted measurement of the air with a capillary flow meter and adjustment of the flow rate to the amount (0.0005 cu. ft. per minute) found to be best by experiment. The temperature of the generator was controlled by placing it inside a cabinet which was electrically heated and regulated by a thermostat at 90°F. The original culture of acetic acid bacteria was obtained as an unpasteurized and unfiltered sample of vinegar from a commercial vinegar manufacturer.

The important finding in the first attempt to make citrus vinegar was the fact that vinegar was made at a satisfactory rate and a satisfactory yield or conversion rate from alcohol to acid was obtained. The generator was kept in continuous operation for 29 months making vinegar from orange, grape-

fruit, tangerine and citrus molasses wines. Most of these products were of good or excellent quality.

Since the recent advent of the "submerged fermentation" process for vinegar manufacture has rendered the generator packed with shavings obsolete, it would seem superfluous to describe in detail all of the experiments carried out with the generator. It is sufficient to say that the generator produced citrus vinegars worthy of further investigation.

Our generator had the disadvantage of having a very small capacity and most of the product was used up in analyses. Furthermore, only one batch could be acetified at one time. In order to enlarge the quantity of citrus vinegar produced and to investigate a large number of variables simultaneously, the slow or Orleans process was used. Nearly 40 gallons of grapefruit vinegar were made in 2 wide-mouth glass jars of 5-gallon capacity. The jars were filled about half full with a mixture of the wine, or fermented juice, and vinegar which contained active acetic acid bacteria. A film of the bacteria formed on the liquid surface. When maximum acetic acid concentration was obtained, about half the vinegar was drawn off and replaced with an equal volume of wine. Care was taken not to disturb the surface film unnecessarily. The vinegar made in this way was excellent and created considerable interest among those receiving samples. Indeed, the Orleans process has the reputation of producing the highest quality vinegar. Its slowness permits the formation of esters that enhance the flavor.

The Orleans process was also used to produce small batches of vinegar from fruit that had been severely frozen during the cold weather of December 1957 and January 1958. The vinegar from this frozen fruit was as good as that from otherwise sound fruit.

The use of the Orleans process for these investigations had the advantage that the batches could be kept small so that less material was required. Furthermore, a number of batches could be in process at the same time. As usually carried out, 100 or 200 ml. of an active vinegar culture was added to 200 or 300 ml. of the wine that was desired to be acetified into vinegar and the mixture was placed in a 3- or 4-quart wide-mouthed bottle or jar. The open mouth was covered with 3 layers of cheesecloth to keep out insects. As acetic acid was produced, more wine was added until the jar was ½ to ⅔ full. When the maximum acidity was reached, the vinegar was filtered, pasteurized

and bottled. Samples for acid determination were removed by inserting a pipette through the surface film. Wine additions were made with minimum disturbance of the film by running the wine down the inside wall of the jar or through a funnel with its stem inserted through the film.

While both the Orleans and the packed generator processes have served very useful purposes in the development of quality vinegars from citrus fruit, the only process that needs to be considered for commercial production at present is submerged fermentation. The increased efficiency of the latter process has made the others obsolete.

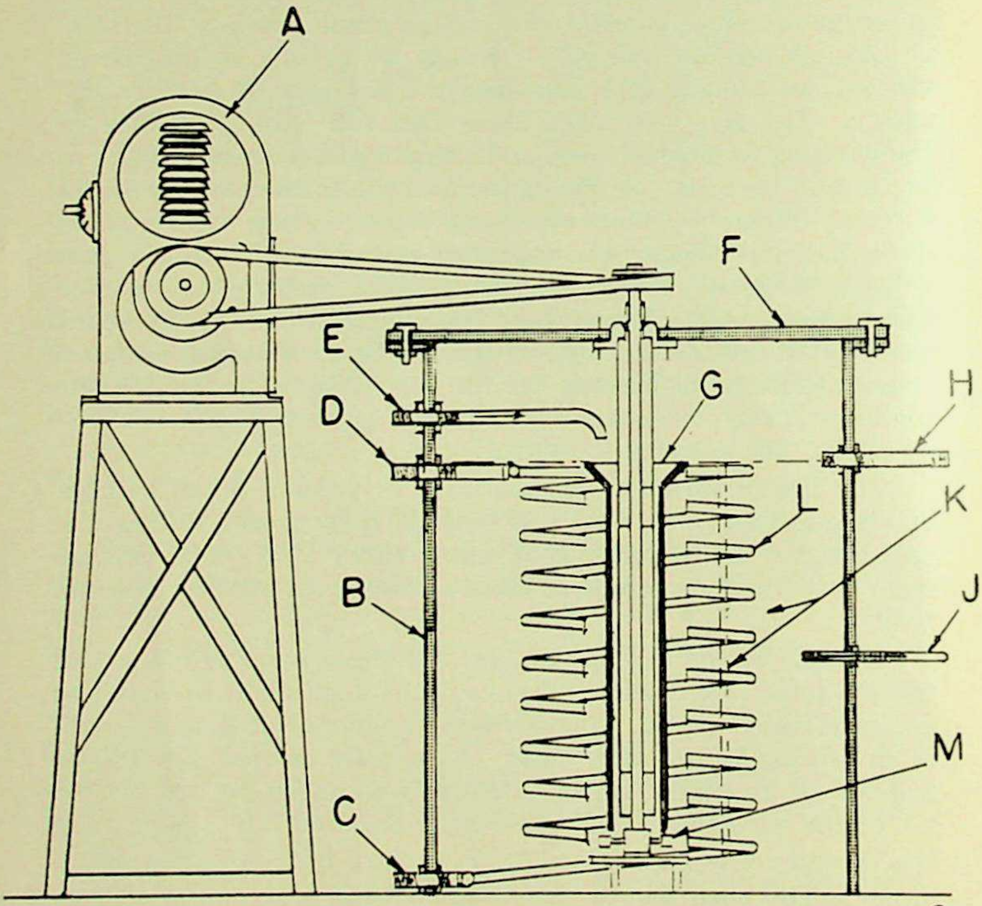

Fig. 1.—Cutaway drawing of the Cavitator. A, variable speed drive; B, clear plastic tank; C, cooling water inlet; D, cooling water outlet; E, feed inlet; F, stainless steel lid; G, draft tube; H, product outlet; J, thermometer; K, plastic baffle; L, cooling coil; M, rotor mounted on hollow shaft.

The fermenter used in the submerged fermentation experiments was a pilot plant model "Cavitator"* consisting of a 20-gallon transparent plastic tank with vertical baffles to stop vortex action of the liquid. A helical coil of stainless steel tubing inside the tank carried cooling water for temperature control. The rotor with its hollow shaft and the draft tube were made entirely of stainless steel and were attached to the stainless steel lid. Rotation of the rotor sucked air down the hollow shaft and dispersed it in fine bubbles in the liquid. Practically instantaneous mixing of the liquid was also produced by the rotor action. Power for driving the rotor was supplied by a ¼ hp. U. S. Varidrive motor.

Figure 1 shows a sectional view of the Cavitator. A Sigmamotor pump with attached speed changer and motor was used to meter the wine feed from the supply tank to the Cavitator. With this equipment it was possible to vary the feed rate from 2 to 20 gallons per day as needed. Tygon tubing was used to transport both wine and vinegar between different pieces of

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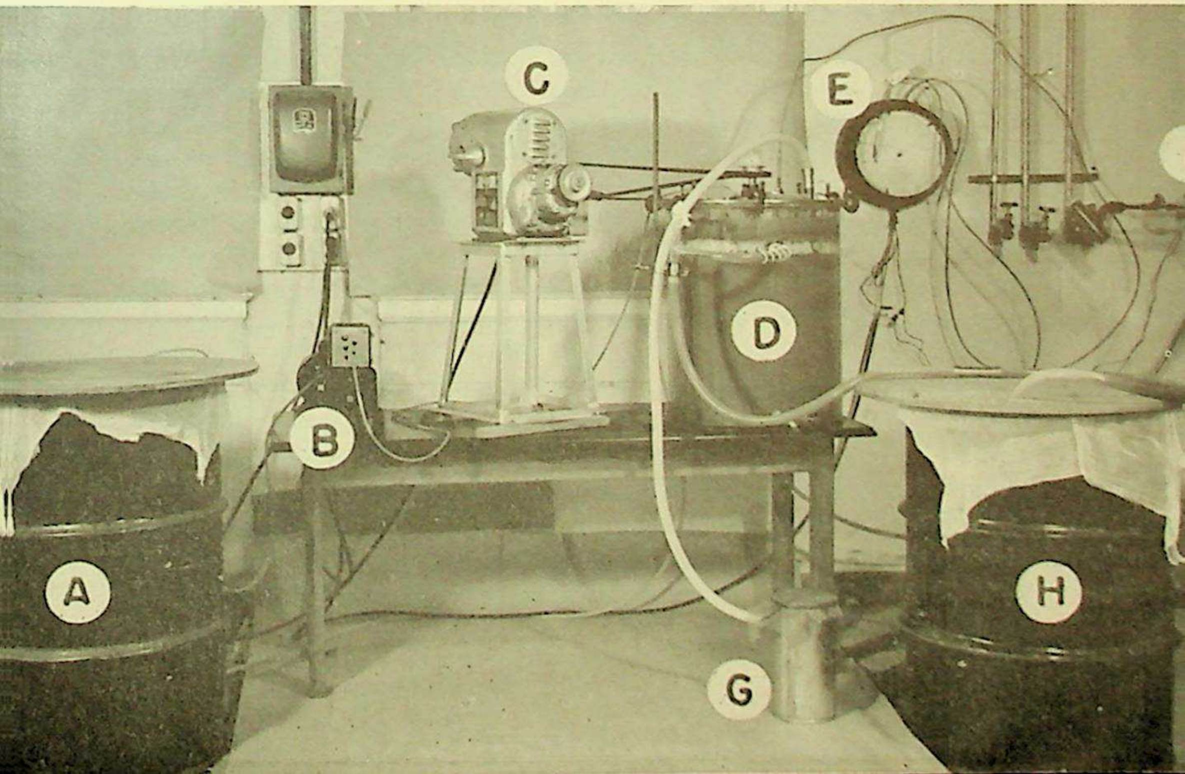
* Registered trademark of Yeomans Brothers Company, manufacturer.

Fig. 2.—Pilot plant for making citrus vinegar. A, feed tank; B, Sigmamotor feed pump; C, variable speed drive; D, cavitator; E, temperature controller and recorder; F, solenoid valve in cooling water line; G, foam trap; H, product tank.



equipment. Feed and product tanks consisted of open-end 55-gallon steel drums with plastic liners made of polyvinyl chloride. Cheesecloth was draped over the open ends to keep out insects and plywood covers prevented appreciable evaporation. Figure 2 is a photograph of the vinegar making assembly.

The first submerged fermentation run was made at a temperature of 90°F., but during subsequent runs 86°F. was maintained. At the higher temperature the bacteria were more active and converted alcohol to acetic acid more rapidly, but they were also much more sensitive to the concentration of alcohol in the acetifying liquid. When the alcohol concentration exceeded about 0.080 percent by weight, conversion to acetic acid was suppressed. When the concentration was below 0.030 percent, the bacteria started to oxidize some of the acetic acid to carbon dioxide and water. Maintenance of the alcohol concentration between these 2 points was a difficult task and demanded constant supervision and frequent alcohol determinations. At 86°F. alcohol concentrations of 0.200 to 0.300 percent were tolerated.

Experience has shown that 0.100 percent of alcohol probably was close to the optimum concentration under the conditions usually encountered in continuous operation. Concentrations of alcohol in excess of the optimum can lead to loss of this material by volatilization in the air stream as well as retarding the bacterial activity.

Approximately 550 gallons of various citrus vinegars were produced by submerged fermentation. The varieties were orange, grapefruit and tangerine juice vinegars and orange peel vinegar. Ordinarily this quantity of vinegar could have been produced in about 40 days of continuous operation with the equipment used. However, to reduce mixing of the different varieties to a minimum, the Cavitator was drained to 5 gallons before starting production of a new variety of vinegar. In this way, mixing of the old variety in the new was held to 5 percent or less.

Starting each time with the Cavitator less than ¼ full required slow rebuilding of the culture and extended the total length of operations to nearly 150 days. If a sufficient amount of the new variety had been available from previous operations to fill the Cavitator at the beginning of the run, an appreciable amount of the starting-up time could have been saved. Acetification efficiency also suffered from this variation in production

rate. Acetification efficiencies of 95 percent or more were encountered only toward the end of each run.

With continuous operation over an extended period there is every reason to believe that production rates and efficiencies in the case of citrus vinegars would be just as high as obtained by Cohee and Steffen (*1*) with cider and other vinegars.

Two different quantities of orange juice vinegar were produced by submerged fermentation. In one, the sugar content of the juice was augmented by the addition of corn sugar before yeast fermentation so that a 60 grain vinegar could be made. Since this material was not heated until final flash pasteurization, the vinegar produced was light yellow. However, on storage, it darkened to a typical amber or brown color. The other quantity of orange juice vinegar was produced from juice that was concentrated to 16° Brix before yeast fermentation. It was noticed that the latter had more characteristic flavor than the former orange juice vinegar. The quality of both was excellent. Excellent vinegar was made also from tangerine juice.

Grapefruit juice vinegar was interesting, not only because of its excellent flavor but also because of the high citric acid content of the original juice, which enhanced the total acidity of the vinegar by almost 40 percent. Indeed, the total acid strength of this vinegar could not be adjusted to below 56 grains without the acetic acid content being reduced to less than 4 percent. Since sourness is the principal characteristic of vinegar, the additional citric acid sourness of grapefruit vinegar may be used to advantage.

Particular mention should be made of the vinegar produced from "press liquor" which is the liquid obtained when citrus peel is ground, treated with lime and pressed. The press cake is dried and sold for cattle feed. The press liquor may be partially evaporated and added to the press cake for further drying or it may be concentrated to citrus molasses and sold as such. Since it contains 6 or 7 percent fermentable sugar, press liquor is a possible raw material for vinegar. It is also practically a waste material and therefore cheap.

The vinegar made from press liquor was darker in color than the other vinegars and had an entirely different aroma and flavor. The aroma was more "fruity" than the other varieties. Whether these differences will be for better or worse remains to be seen.

The name "orange peel vinegar" has been tentatively used here, since it was believed "press liquor vinegar" was not prop-

erly descriptive and might be misinterpreted. In the present case only orange peel was used in the production of the press liquor. Had a mixture of orange and grapefruit peel been used, the product would have been called "citrus peel vinegar."

The lime treatment of the ground peel during the production of press liquor neutralizes practically all of the free organic acids present. Consequently, the sourness of citrus peel vinegar is derived almost entirely from the acetic acid present.

TABLE 1.—TYPICAL FREE ACID CONTENT OF CITRUS VINEGARS.

Type Vinegar	Percent Total Acids	Percent Citric Acid	Percent Acetic Acid
Orange vinegar	5.07	0.87	4.20
Grapefruit vinegar	5.60	1.52	4.08
Tangerine vinegar	5.00	0.62	4.38
Orange peel vinegar ..	5.00	0.00	5.00

At times foaming has been a problem in making vinegar by submerged fermentation (*1*), but it can be controlled by antifoam agents. Citrus vinegars were no exception but their foaming tendencies were not excessive. Citrus peel vinegar from press liquor did foam somewhat more than that made from juices. It was noticed that foaming was more pronounced when the feed rate to the fermenter was equal to or somewhat in excess of the capacity of the culture to convert the alcohol into acetic acid. Maximum production from a fermenter doubtless would require the use of some antifoam at all times. When maintained in a slightly "starved" condition, the submerged fermentation can be operated without using antifoam.

The Acetic Acid Bacteria.—As stated previously, the original culture came from a commercial source. This sample was used to inoculate the packed generator. All of the Orleans process batches were inoculated from vinegar made in the generator and the Cavitator was inoculated with bacteria from Orleans process vinegar. Since vinegar is a low cost and competitive product, the expense of maintaining and using pure cultures cannot be justified in commercial practice.

Fortunately, few organisms can survive the conditions in vinegar generators and those that do seldom cause trouble. Adhering to commercial practice, no attempt was made to exclude air-

borne microorganisms in making citrus vinegars. There is reason to doubt, therefore, that all batches were produced by the same strain of bacteria. Microscopic examination of the culture at different times did show differences in morphology, especially during the submerged fermentation experiments. At one time, when the temperature of the Cavitator reached 92°F. for several hours, due to malfunction of the controller, the bacteria were all small diameter diplococci. Ordinarily they were short, rod-shaped bacilli but not always uniform in diameter. The different appearance of the bacteria at different times may have been pleomorphic phases of the same strain or the predominance of different strains under varying conditions. It apparently is not important to know the answers to these questions in practical vinegar making.

Effect of Peel Oil.—All citrus juices contain a small amount of an essential oil which in trade parlance is generally referred to as "peel oil" because nearly all of it is found in the peel of the fruit. This oil is responsible for a considerable portion of the characteristic flavor and aroma of citrus juices. It is also responsible for some of the off-flavors that may develop when citrus juices are mishandled.

The initial feed for the generator consisted of a batch of orange wine. The wine was obtained from orange juice which was brought to 16° Brix by the addition of sugar before fermenting with a wine-type yeast. After fermenting, the wine was stored at room temperature for several months. During storage, it darkened and developed a "terpeney" or "furniture polish" odor and taste. It was not known, at first, whether this flavor would carry over into the finished vinegar. This wine would not have been used except for the fact that it was the only fermented citrus juice on hand at the time that the culture of vinegar bacteria arrived and it was feared that the activity of the culture might be lost if it were not put to work immediately.

The packed generator was started, using this batch of off-flavored wine. It was found that the off-flavor persisted and a vinegar was produced that probably would have limited acceptability. The peel oil in the original juice was suspected as the source of off-flavor and subsequent experience has proved this to be so.

It had been found (*5*) that complete removal of peel oil from citrus juices could be achieved by adding an equal volume of ethyl alcohol to the juice and then distilling off the alcohol. The

peel oil was carried over into the distillate. A few liters of orange juice were treated in this manner to remove the oil and then fermented with yeast and finally made into vinegar by the slow process. Even after months of storage there was no evidence of the development of off-flavor. This treatment, while effective, naturally was too cumbersome for a practical de-oiling procedure.

It has been known for a long time that peel oil is attached to or intimately associated with the pulp or suspended particles in citrus juice. Any procedure that reduces the amount of pulp in the juice will reduce the amount of oil. A "soft squeeze" during the extraction of the juice from the fruit and passing the juice through a finisher with a fine screen are helpful. Also, partial evaporation of the juice either with or without vacuum will reduce the oil content. None of these operations, however, will entirely remove the oil.

Peel oil and its effect can be eliminated by passing the juice through a finisher with a fine screen (0.02" holes or less), followed by evaporation to about ⅔ of its volume and then fermenting with Bakers' yeast using a substantial volume (5 to 10 percent) of starter. As soon as the fermentation activity slows down and the yeast settles (3 to 5 days), the supernatant liquor is decanted and filtered so that only haziness remains. If filtration is delayed, the blanket of carbon dioxide above the liquid surface becomes dispersed, allowing oxygen from the air to reach the remaining peel oil. Oxidation of the peel oil produces the "terpeney" flavor which cannot be removed effectively.

The amount of peel oil present in press liquor should receive special mention. As obtained from the presses, this liquor contains relatively large amounts of oil, sometimes exceeding 1 percent by volume. The most practical method of rendering the liquor suitable as a raw material for vinegar was found to be heating it to 180° to 200°F., allowing it to stand several hours and drawing off the portion that is fairly free of suspended solids. About 60 to 70 percent of the original volume thus obtained can be filtered clear without much difficulty. The remainder may be returned to the molasses operation.

The filtered liquor can be evaporated at atmospheric pressure or under vacuum to the desired concentration before fermentation and acetification. After acetification, the vinegar should be pasteurized before final filtration since heating the vinegar usually causes some additional material to precipitate, resulting in a cloudy or hazy product.

Use of Pectic Enzymes.—Another problem encountered in the production of citrus vinegar was that of obtaining a clear product. Turbidity and cloudiness are expected and protected in citrus juices but must be eliminated in vinegar made from them. The pectic substances present make filtration painfully slow.

The juice normally contains an enzyme, pectinesterase, which removes the methoxyl groups from the pectin molecule. This action, however, is not enough to make the juice readily filterable. There are available a number of commercial enzyme preparations derived from certain molds that will hydrolyze pectin all the way to galacturonic acid. Citrus juices treated with these enzymes can be filtered with reasonable amounts of filter-aid to produce a clear liquid that contains no peel oil and therefore can be used to produce a vinegar that is free of off-flavors.

The rate of reaction of these enzymes is relatively slow and it has been found advantageous to allow them to act at the same time that yeast is fermenting the sugars of the juice to alcohol. Since the yeast fermentation requires from 3 to 5 days, this extended period permits the use of minimum amounts (about 0.01 percent by weight) of pectic enzymes to destroy the sliminess of the juice. This is a great advantage. Furthermore, pectic enzymes are relatively expensive and the quantities should be held to a minimum in any event.

TABLE 2.—METHANOL CONTENT OF CITRUS VINEGARS.

Type Vinegar	Percent Methanol by Weight
Tangerine vinegar	0.010
Orange vinegar	0.010
Grapefruit vinegar	0.0094
Grapefruit vinegar	0.0096
Citrus molasses vinegar	0.0078

A side effect of the use of pectic enzymes was found to be the release of methanol in the juice due to the splitting-off of methoxyl groups. While methanol is a poison when ingested in appreciable amounts, the quantity found in citrus vinegar was not believed to be of any significance. Nevertheless, it was

thought that the quantities found should be recorded to forestall exaggerated inferences in the future. Table 2 gives the results of analyses of several different batches of citrus vinegar. Apparently the methanol content of citrus vinegars runs in the neighborhood of 0.01 percent. As far as known, there is no established limiting concentration of methanol in vinegar.

The first few times pectic enzymes were used care was not taken to add only the minimum amount required to hydrolyze the pectin. After the vinegar was finished and stored for several weeks, a brown sediment appeared in the bottles. The sediment was soluble in dilute sodium hydroxide solutions and was reprecipitated upon acidification. It gave negative tests for carbohydrate. It contained 4.87 percent nitrogen, indicating that it might be a protein. Hydrolysis to amino acids was found to be difficult, but was finally accomplished by heating the sediment in a sealed tube at 150°C. with 20 percent hydrochloric acid. Analysis of the hydrolyzate by paper chromatography revealed the presence of 11 amino acids. By this time the pectic enzyme preparation was suspected as the source of the sediment. When a sample of the enzyme was treated in the same manner, the pattern of amino acids on the paper chromatogram was so strikingly similar that there was no doubt that the sediment was derived from the enzyme added. A molecular weight determination of the sediment gave a value of 3,000,000 to 5,000,000, whereas unused enzyme gave 90,000.

Apparently in the finished vinegar, the spent enzyme gradually polymerizes to a large molecule that is no longer soluble and therefore precipitates as sediment. The slowness of precipitation may be judged by the fact that 4-year-old vinegar showing sediment was filtered clear and stored in a clean bottle. In a few weeks additional sediment formed. The presence of the sediment is objectionable only because of its unsightliness which would reduce the salability of the product.

Because of this undesirable effect of the pectic enzyme preparation that was used, a survey was made of available commercial pectinases to determine if there were any that did not cause sediment formation. Small quantities of vinegar were made by the Orleans process using each of the different commercial samples. Considerable variation was found among the 14 different preparations, both in their ability to hydrolyze pectin in the juice and in their sediment-forming tendency. All enzymes but 1 produced some sediment in vinegar after 6 months storage

when used at concentration of 0.25 percent or more. There were a few that had adequate pectinase activity at concentrations of 0.015 to 0.020 percent by weight, yet did not give rise to sediment formation at this level after 6 months storage.

An additional benefit from the use of pectic enzymes may be found in their ability to hydrolyze the flavonoid glucosides that occur in citrus products. For example, the glucoside naringin is found in grapefruit and is responsible for the characteristic bitterness of this fruit. Similarly, hesperidin is found in oranges but is flavorless or nearly so. Ordinarily the bitterness of naringin in grapefruit vinegar is suppressed by the sourness of vinegar and is not noticeable at usual concentrations. Nevertheless, 1 batch of grapefruit vinegar was prepared from ground whole fruit with the result that the naringin content exceeded saturation concentration in the product. Some of the glucoside precipitated out on storage. Also, a batch of orange vinegar was made that developed a precipitate of hesperidin on storage. In cases such as these, hydrolysis of a portion of the glucoside by enzyme action would protect the appearance of the product.

The different enzyme preparations that have been tried had widely varying glucosidase activities. Selection of the most suitable preparation would therefore be important.

ECONOMIC ASPECTS

The quality of vinegar made from orange, grapefruit and tangerine juices appears to be exceptionally good. Most people who have been given samples have returned for more. A number of food editors of national publications have praised them highly. Samples sent to one of the largest chains of supermarkets in the country were evaluated by their taste panel and judged superior to cider vinegar and were said to have an interesting and distinctive flavor.

In spite of these favorable expressions, the place that citrus vinegar might achieve in commercial channels can be determined only by further market research. Should public acceptance be favorable in comparison with wine vinegars, it would be possible to manufacture citrus vinegar at a fairly good profit but with a somewhat restricted market. Should it be possible to produce citrus vinegars as cheaply as cider vinegar, a truly large market would become available. Without a background of full-scale oper-

ating experience, there is a reasonable doubt that citrus vinegars could compete on an equal cost basis with cider vinegar.

Citrus peel vinegar should be considered separately, since its flavor is entirely different from that made from juices. Also, samples of this material have not had wide distribution and opinions on its quality are not yet available.

While it is possible for one to become enthusiastic about citrus vinegars from a quality standpoint, a consideration of costs of production may have a temporizing effect. In the discussion here, a different basis has been used for determining the cost of the raw material for making orange, grapefruit, tangerine and citrus peel vinegar. The disadvantage of this presentation is realized. Nevertheless, the derivation of these figures is based on current practices of the citrus industry.

For example, most oranges are now purchased on the basis of a given price for each pound of solids in the juice. This has become customary since the great expansion in the production of frozen orange concentrate. Grapefruit and tangerines, still largely fresh fruit items, are purchased on the basis of a field box. Variations in juice yield and sugar content do not affect the price proportionately. Citrus peel juice, known in the industry as "press liquor", can be purchased on a gallon basis which is not directly dependent upon the original fruit cost.

Recently orange juice suitable for frozen orange concentrate production sold for 65 cents per pound of juice solids based on the Brix determination. In other words, a juice having a Brix reading of 11° would be considered as containing 11 percent juice solids. About 70 percent of orange juice solids are fermentable sugars, hence 65 cents would buy 0.7 pound of these sugars. When fermented with yeast, the sugars yield just about 50 percent by weight of alcohol. The 65 cents would therefore buy 0.35 pound of alcohol which, when acetified, would make 0.46 pound of acetic acid. This, in turn, would produce 11.5 pounds of 40 grain vinegar. The 11.5 pounds of vinegar would be equivalent to 1.35 gallons. The raw material cost for 40 grain orange vinegar would then be 65/1.35 or 48 cents per gallon. This would be entirely too high-priced except possibly for the small volume that might be sold at high prices to the gourmet trade.

These figures are admittedly on the extreme side; 65 cents per pound of juice solids is a very high price and is not expected to remain at this level. Nevertheless, more normal prices of 40 to 45 cents per pound of orange juice solids are believed

sufficiently high to eliminate orange juice as a source of vinegar on a large scale. On the other hand, there are always available moderate amounts of fruit and juice that, for one reason or another, cannot demand maximum price. Much of this might well be channeled to vinegar production.

In the case of tangerines, a large portion of the crop is seldom harvested because of small size or maturity after peak demand has passed. Doubtless, a considerable quantity of tangerines could be obtained for little more than harvesting costs. Excellent vinegar has been made at the Citrus Experiment Station from somewhat over-mature tangerines. From 75 field boxes of tangerines, 126½ gallons of 50 grain vinegar were made. The yield of 1.68 gallons per box was less than expectation. It was due to the low yield of juice as the result of using improper extraction equipment. Normally the yield of vinegar could be twice as much. Assuming a price of 30 cents per box of tangerines and a yield of 2.52 gallons of 50 grain vinegar per box, or 50 percent more than above, the raw juice cost of the vinegar would be 13.5 cents per gallon. This compares favorably with a raw material cost of 10.9 cents per gallon for vinegar made from corn sugar. The latter is a white vinegar of lower quality than citrus vinegar.

Grapefruit, because of its naturally higher acidity and normally lower cost than oranges and tangerines, deserves individual consideration as a source of vinegar. The citric acid content of the juice is normally 0.9 to 1.5 percent. When partially concentrated so that the final product will have at least 4.0 percent acetic acid, the citric acid content may be 1.5 percent and sometimes more. A 60-grain vinegar then can be made that has only 45 grains of acetic acid. Since sourness is the major characteristic of vinegar, the citric acid in citrus fruit may be used to advantage, especially in the highly acidic grapefruit. It is estimated that adequate supplies of low grade grapefruit can be obtained for 50 cents or less per field box. From this, it should be possible to make about 3.5 gallons of 60 grain vinegar. The raw material cost on this basis would be 14.3 cents per gallon.

Also deserving individual consideration is citrus peel vinegar made from press liquor. Free citric acid here is negligible because of lime treatment during manufacture. On the other hand, its low price of approximately 1.5 cents per gallon and its fermentable sugar content of about 6 percent should make possible the production of a low cost vinegar. Even though one third of

the liquor is discarded with the majority of the suspended solids as explained earlier, the cost per pound of fermentable sugar would be approximately 4.5 cents, which is less than the price of corn sugar. Should the vinegar operation be charged with only the proportion of liquor actually used, the cost per pound of fermentable sugar is only 3.4 cents per gallon. Based on these raw material costs, citrus peel vinegar should be competitive with all other vinegars except possibly "distilled" vinegar. It should be mentioned, however, that improved sanitary conditions should prevail in the production of press liquor to be made into products intended for human consumption. This may increase its cost somewhat.

It is probable that processing costs of citrus vinegars may be somewhat higher than other vinegars because of the extra filtration required to avoid the effects of peel oil. Filter-aid requirement for this filtration is estimated at not over 1.0 cent per gallon and enzyme requirement at 0.6 cents per gallon. Power and labor costs may bring the extra filtration cost up to 2.0 cents or possibly 2.5 cents per gallon, depending upon the volume of production. These figures may be excessive, since reliable sources have stated that vinegar can be made on a large scale for 2.0 to 4.5 cents per gallon, not counting the raw material.

Vinegar making is traditionally a competitive business based on large volume and low profit margins. Production of wine vinegar is a possible exception, since it is relatively new and the volume is not large. Orange vinegar has the least chance of successfully competing on a price basis with established products, unless the juice can be obtained at distress prices. Grapefruit and tangerine vinegars have interesting possibilities, since it is likely their juices can be obtained at low cost at certain times of the year. Citrus peel vinegar has great possibilities as far as costs are concerned, but remains to be tested for public acceptance.

Ordinarily citrus juices do not contain sufficient fermentable sugar to yield 4 percent acetic acid in the finished vinegar without partial concentration or the addition of some sugar. The addition of sugar to citrus juices intended for canning is permitted within limits as long as this fact is mentioned on the label. It is not known whether the addition of sugar to juice intended for vinegar making would be legal. Perhaps it would be allowed if no additional water were added to adjust the grain strength. Using sugar in this manner would reduce costs in

porportion to the amount added, since cane sugar is cheaper per pound than the sugars in citrus juices. In the case of citrus peel vinegar, however, the added sugar would be more costly per pound than the sugar in the press liquor. Adding sugar here would therefore be wasteful.

A batch of orange vinegar was made by submerged fermentation from juice that was fortified with sugar before fermentation. The product was completely satisfactory, but on direct comparison with orange vinegar made from partly concentrated juice, there was a noticeable dilution of flavor. Carried to extreme, the addition of a large amount of sugar followed by water after acetification could lead to a vinegar with no more flavor than white vinegar.

FEDERAL REGULATIONS

Since vinegar can be made only from an alcoholic liquor, Federal regulations must be followed. In reply to an inquiry, the Internal Revenue Service stated "—vinegar produced by acetification of wine would first require the manufacturer to qualify a bonded wine cellar and thereafter to remove the wine free of tax for use in the manufacture of vinegar." Part 240 of Title 26 (1954), Code of Federal Regulations, entitled "Wine", covers the qualification of bonded wine cellars. In particular, Sections 240, .120, .130, .225 and .650 through .662 are concerned with the qualification of a bonded wine cellar and subsequent removal of wine for the production of vinegar. Part 195 of title 26 (1954), Code of Federal Regulations, entitled "Production of Vinegar by the Vaporizing Process," should also be consulted. In order to avoid violations it would be wise for anyone planning to enter into the manufacture of citrus vinegar to become familiar with these and all other applicable regulations before proceeding with construction or allotment of manufacturing space.

CONCLUSIONS

It is the opinion of many that the quality of citrus juice vinegars is such that they should have a place in the vinegar industry. Just where that niche may be can only be determined by marketing trials. It is believed they compare favorably with wine vinegars now being marketed, but only the public can confirm this. Until cost figures from commercial operations are available, conservative estimates indicate that citrus juice vinegars cannot be manufactured as cheaply as cider vinegar. On

the other hand, citrus peel vinegar should be a low cost item. Whether its flavor would be acceptable as a table vinegar or whether it would be useful in prepared foods, sauces, dressings, etc., remains to be seen.

The special characteristics of citrus juices and liquids due to the presence of peel oil and pectin can lead to difficulties. Unless eliminated early in the vinegar process, peel oil will become altered and give rise to undesirable off-flavors in the final product. Pectin interferes with the production of a clear product. It can be eliminated by the use of hydrolyzing enzymes. However, undesirable sediment may form in the vinegar from the spent enzyme. Also, traces of methanol have been detected in vinegar made with the help of pectic enzymes. The methanol was derived from the methoxyl groups of the pectin molecule. It is believed that the necessary and sufficient conditions of operation have been described in this bulletin.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of the following persons. Dr. R. F. Cohee, Food Technologist, Wheaton, Illinois, for his encouragement and technological help, especially during the early portion of the project. Mr. Grover Steffen, President, M. Steffen Company, Chicago, Illinois, for supplying the original culture and beechwood shavings used in the packed generator and for many courtesies during a visit to the Chicago plant. Mr. D. W. Burgoon, President, Yeomans Brothers Company, Melrose Park, Illinois, for the loan of a pilot plant model Cavitator for the submerged fermentation studies. Mr. William Lawson, Feed Mill Foreman, Adams Packing Association, Inc., for assistance in obtaining press liquor of the desired type. Jacques Wolf & Co., Rohm & Haas Co., Takamine Laboratories, and Wallerstein Laboratories for supplying samples of pectic enzyme preparations. Many employees of the Citrus Experiment Station for extracting and concentrating the fruit juices when needed.

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